SELECTED PROPERTIES OF GEOPOLYMERS WITH DIFFERENT PORTIONS OF GROUND FLY-ASH

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Abstract

Geopolymers are polymeric materials resulting from the polycondensation reaction of alumino-silicate materials in a strongly alkaline environment. In consequence, stable polymeric networks of aluminosilicates are formed. The binding potential of FA (fly ash) amorphous component can also be "activated" by mechanical activation, which unfolds new possibilities of FA utilization. Mechanical activation, such as the method, which can improve FA reactivity, is often applied for different applications for geopolymers based on ground fly ash. This paper presents possibilities of preparation of geopolymer mixtures based on modified (ground) FA (TEKO – produced by the Heating plant Kosice), which was used in varying percentages to unground (original) FA. The particle size of the original unground FA (PVT) was 84.7µm and particle size of the ground FA (T60S1) was 52.8µm. Properties to be evaluated were selected from the expected application point of view – protective coating of concrete. Next properties of geopolymer mixtures after 28 days of hardening were tested and evaluated: dry density, absorptivity, capillarity, compressive and flexural strength.

Keywords: geopolymer, fly ash - FA, strength, absorptivity, capillarity

1 INTRODUCTION

Civil engineering industry provides big and significant amount of options for use of industrial wastes in manufacturing of some building materials, or in the development of new ones. Global development of consumer society, however, leads to an enormous increase in waste production and problems with their disposal, therefore the necessity of processing the wastes even at higher energy expense and final cost is discussed still more and more (Rai A. and Rao D.B.N., 2005).

Worldwide, millions of tons of fly ashes are generated each year by coal-fired power plants satisfying the large demand for industrial and domestic energy. In Slovakia, a majority of fly ashes is hydraulically transported to the settling basins or extracted mines, and only a small amount of fly ashes is utilized. The deposited fly ashes are being exposed to exogenous and biogenous factors that change their chemical and structural composition and become harmful to the environment (Michalíková et al., 2003). Therefore, large numbers of researchers have been focused on utilization of this waste material. Nowadays, waste materials or pozzolans from industrial and agricultural by-products, such as fly ash and rice husk ash, are receiving more attention, since their uses generally improve the properties of the blended cement concrete, lower the costs, and reduce the negative environmental effects (Rukzon and Chindaprasirt, 2008; Chindaprasirt et al., 2008).

Moreover, it is a well known fact in the field of construction materials that potential of some secondary raw materials can be significantly increased and used after their adjustment. The result is higher extent of valorization even of the wastes that were not suitable in their original form. At the same time, parameters are improved, or new parameters appear.

Fly ashes in a fine grain form can be used in concretes as:

- additive
- component of inorganic materials for secondary protection of the concrete.

By applying both classic and unusual adjustment methods it is possible to modify parameters of fly ashes to improve them for a particular purpose of use. Adjustment of fineness of the particles is one of the ways to improve usability of wastes and possible improvement of building materials parameters (Želinková et al., 2013; Želinková, 2014).

One of the ways how to use fly ash is preparation of geopolymer mixtures. Geopolymers fall into the class of aluminosilicate binding materials synthetized by alkali activation of solid aluminosilicate raw materials, such as fly ash, GGBS (ground granulated blast furnace slag), etc., with an alkali metal hydroxide and silicate solution. Utilization of fly ash in the development of geopolymeric materials for construction purposes was and still continues to be a subject of many research studies (Balaguru et al., 2004; Davidovits, 2008; Ravindra and Ghosh, 2009; Temuujin et al., 2010).

The effect of the fineness of fly ash on geopolymer materials properties is also widely discussed. Changes induced in material during the mechanical activation process include reduction in particle size, changes in particle morphology, increase in specific surface area, structural defects formation, decrease in crystallinity degree, implying structural rearrangement. The most important consequence of transformation that occurs in material during the mechanical activation is its enhanced reactivity. Mechanical activation, as a method, which can improve FA reactivity, is often applied for different applications of this material. Improved reactivity is primarily the result of increased particle fineness and formation of amorphous regions in the structure. Finer particles of FA provide more reactive material without extra mechanical treatment. It is known that particles below 45 μm, obtained through various methods of separation, tend to improve the mechanical strength of the mortar when used as a supplementary cementitious material (Marjanović et al., 2014). Although numerous data exist relating to the mechanical activation of FA, the literature concerning the application of mechanically activated FA for the geopolymer synthesis is rather scarce. The main advantage of using mechanically activated FA in synthesis of geopolymers is the possibility of total utilization of FA, and not only its specific (finer) fraction.

This paper deals with the possibilities of preparation of the geopolymer mixtures based on modified (ground) fly ash, which was used in specific percentage combinations with unground (original) fly ash. As a modification, sludge from the process of washing of the crushed aggregates was used in-the next mixture as a filler. Finally, standard cement mixture using the same filler was prepared for testing. The results were analysed in the terms of possible application to protect the concrete surface by coating.

2 MATERIALS AND METHODS

The materials used for tested mixtures were as follows:

- Original fly ash - PVT (from the Heating plant Kosice). The calcium oxide content of the fly ash is less than 10%; hence it can be classified as the Class F according to the ASTM 618 standard,
- Ground fly ash - T60S1: the same fly ash (time of grinding: 60 minutes, grinding ratio – mass of ground material to mass of grinding balls: 1/17),
- Ground granulated blast furnace slag (GGBFS): as geopolymer intensificator,
- Na_2SiO_3+ NaOH as geopolymer activator,
- Sludge, material from the process of washing of the crushed aggregates, coming from the sludge bed of the IS - Lom s. r. o, Maglovec,
- Ordinary Portland Cement (CEM I 42.5 R, Holcim, Turna nad Bodvou).

Granulometric and chemical composition of fly ashes, GGBFS, cement, sludge (fractions under 125 μm sieved from the unground sludge) are given in Tab. 1 and also in Tab. 2 (granulometric composition of the unground sludge by sieving). -Granulometric composition is expressed by the following parameters – grain size: d (0.1) – indicates that 10% of the whole amount of the investigated sample is under the measured value of the particle size and the similar parameters d (0.5) – 50%, d (0.9) – 90% and the parameter d_m - mean particle diameter.

Table 1. Chemical composition and results of granulometric analysis of the input materials

	Oxide Composition [%]							Grain size [μm]			
Materials	**SiO_2**	**CaO**	**MgO**	**Fe_2O_3**	**Al_2O_3**	**TiO_2**	**K_2O**	**d(0.1)**	**d(0.5)**	**d(0.9)**	**d_m**
PVT (unground)	51.11	2.58	1.18	6.40	23.21	0.96	1.81	3.97	20.44	84.73	74.10
T60S1 (ground)	49.72	2.49	1.09	6.37	22.32	0.94	1.73	3.48	14.53	52.81	31.02
GGBFS	41.28	35.98	12.85	0.39	6.30	0.60	0.54	3.61	19.03	111.5	49.46
Cement	19.87	64.36	4.61	3.18	3.99	0.21	0.30	3.20	17.69	49.57	29.90
Sludge under 125 μm	42.66	5.83	5.04	6.54	11.19	1.72	0.98	17.49	82.50	149.8	83.55

Table 2. Granulometric composition of sludge

Fraction [mm]	Mass yield [wt. %]
2 – 1	20
1 - 0.5	14
0.5 - 0.25	21
0.25 - 0.125	21
<0.125	24

Composition of mixtures was designed on the base of various literary sources (Yazici et al., 2012; Rangan, 2008; Škvara et al., 2005; Palomo et al., 1999; Palomo et al., 2011). The basic geopolymer mixture was intended as microfiller in the terms of alkali-activated fly ash. Alkaline activating agent for as the mixtures T1 – T4 was prepared by mixing the Na_2SiO_3, NaOH and GGBFS. The SiO_2 to Na_2O ratio (Ms Module) in the alkaline activating agent was adjusted by 8 M NaOH addition to Na_2SiO_3 with a module Ms = 2.5. Design of the combination Na_2SiO_3 and NaOH for preparing the activator and its ratio to the other components in mixtures is given in Tab. 3, as well as recommendations summarized from various research reports (Yazici et al., 2012; Rangan, 2008; Škvara et al., 2005; Palomo et al., 1999; Palomo et al., 2011).

Table 3. Conditions of preparation of geopolymers

Parameters		Relationship between the geopolymer components					
		Recommendations according to literature	Investigated mixtures				
			T1	T2	T3	T4	T5
1	Water from the alkaline activators /geopolymer solids; l/s	0.19	0.19	0.19	0.19	0.25	/
2	Alkaline solution/fly ash	0.25-0.45	0.38	0.38	0.38	0.56	/
3	Na_2SiO_3/NaOH	1-1.25	1.18	1.18	1.18	1.18	/
4	water/solids	0.23-0.51	0.24	0.26	0.30	0.33	0.37

Representation of individual components and percentage of constituents in the tested mixtures T1 – T5 are characterized in Table 4.

Table 4. Composition of experimental geopolymer mixtures

Composition of fillers		Mixtures				
[%]		T1	T2	T3	T4	T5
Ground fly ash	46% of mixture volume	100	50	-	70	70
Unground fly ash		-	50	100	-	-
Sludge		-	-	-	30	30
Presence of other components						
GGBFS	20% of fly ash	•	•	•	•	-
Na_2SiO_3	16% of fly ash	•	•	•	•	-
8M NaOH	16.5 % of fly ash	•	•	•	•	-
Cement		-	-	-	-	•
Water		•	•	•	•	•
Plasticizer		•	•	•	•	•

The samples with the dimensions of 40x40x160 mm were kept at the laboratory temperature in the environment with the relative humidity of 50% for 28 days; dry bulk density, compressive and flexural strength, absorptivity and capillarity, were then determined. In accordance with standards, the methods of testing of mixtures were as follows:

- **Dry bulk density** (STN EN 1015-10, 2001)
- **Compressive and flexural strength** (STN EN 1015-11, 2001)

Sorption properties were tested in view of the intended function of the tested materials: protective coating of concrete structures.

- **Absorptivity and capillarity** (STN 73 1316, 1989)

Absorptivity

After drying to constant mass, whole body of the sample was immersed into water. After saturation of the sample to constant mass the specimen was weighted. Absorptivity was calculated by use of the formula (1):

$$\upsilon = \frac{m_s - m_d}{m_d} * 100 \tag{1}$$

where:

m_s – weight of the saturated sample (g)

m_d – weight of the dry sample (g)

Capillarity

After drying to constant mass, one face of the specimen ~~is~~ was immersed into 5 to 10 mm of water for a specific period of time and the increase in mass was determined. Standard periods were 10 min. and 90 min., the following intervals were determined and measured for this experiment: 5, 15, 25, 35, 45, 55, 65, 75, 85, 90 minutes. Capillarity was calculated by use of the formula (2):

$$\upsilon_r = \frac{m_s - m_d}{m_d} * 100 \tag{2}$$

where:

m_s– weight of the saturated sample (g)

m_d – weight of the dry sample (g)

As an additional method for comparison, capillarity as a result of height, to which water soaked (in cm), was tested during the previous test. The results were determined as the arithmetic mean of measurements on 4 sides of the samples.

3 RESULTS AND DISCUSSION

The results of bulk density, water absorptivity and strengths are indicated in Table 5. The values of density are in the range of 1480 - 1760 kg/m^3. The values of water absorption are in the range of 15.17- 20.93 %. The sample with the highest value of density (T4) has the lowest value of water absorptivity. The trend of increasing water absorptivity with decrease of density is in accordance with the known literature data. Values of compressive and flexural strength of investigated samples were in the ranges of 15.75 – 5.44 MPa (R_c) and 1.62 – 3.93 MPa (R_f). Results of compressive strength, and principally also results of flexural strength, confirm the known tendency as well – the values increase with the increasing density.

Table 5. Density, water absorptivity, capillarity, compressive strength R_c and flexural strength R_f (28 days)

Sample	Bulk density [kg/m^3]	Water absorptivity [%]	Capillarity [%] after 90 minutes	Strength	
				R_f [MPa]	R_c [MPa]
T1	1744	15.25	4.45	2.19	11.64
T2	1515	18.11	5.25	1.62	5.72
T3	1477	20.93	6.45	2.45	5.44
T4	1761	15.17	4.08	3.93	15.75
T5	1639	19.75	4.30	2.71	11.36

The following findings resulted from the assessment of the properties of the samples T1 – T4:

- Values of compressive strength and density of the samples based on fly ash are increasing from the sample T3 after the sample T1 (in terms of using the share of the ground samples of fly ash in the mixture), while water absorption and capillarity decreases.
- The sample T4 (substituting 30% of the ground fly ash by sludge) compared to the sample T1, shows in fact the similar value of bulk density, as well as values of the water absorption and capillarity. Sludge in the mixture T4 caused a slight increase in compressive strength of approx. 3 MPa; the sludge had positive effect on increasing the value of compressive strength.

The following findings resulted from the assessment of the the samples T1 – T4 with a reference sample T5:

- In terms of strength: the sample T1 achieved approximately the same strength value (11-12 MPa). The presence of sludge in the recipe T4 caused an increase of compressive strength approx. by 25%. T1 and T2 reached only the half value of the compressive strength compared to T5.
- In terms of absorptivity: the value of water absorptivity of the sample T4 was the lowest of all investigated samples (15%). The reference sample T5 had approximately the same value of absorptivity as the sample T3 (20%).
- In terms of capillarity: capillarity of T5 is approximately on the same level as T1 (4.3%).

Results of capillarity expressed by height of saturation are given in Figure 1.

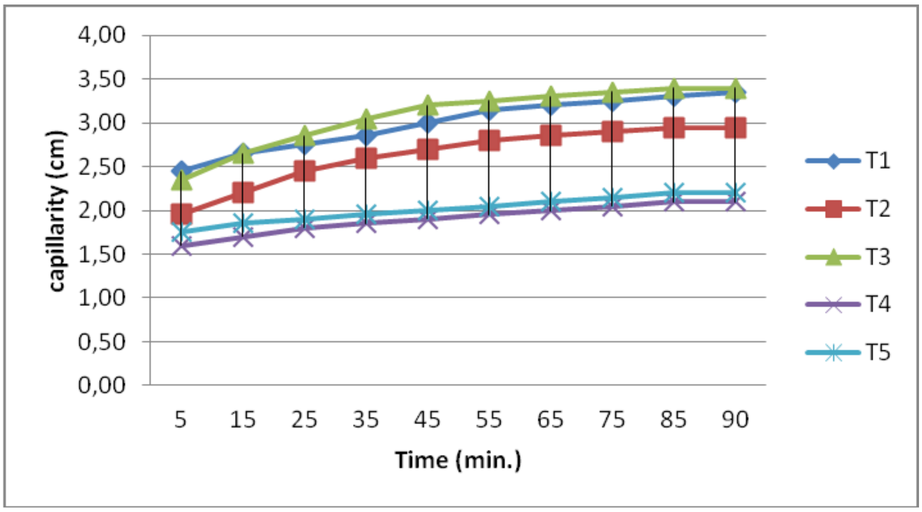

Figure 1. Results of capillarity expressed by height of saturation in cm (28 days)

As it can be seen in Figure 1, the lines of values of capillarity are divided into three sections. The first section contains the value of capillarity for the samples T1 and T3, in the middle part it is T2 and the last part contained the resulting values for T4 and T5. It was caused by the components used in the recipe with various percentage ratios. The specimens T1 and T3 had similar composition – the main component was fly ash (100% fly ash in mixture). T4 and T5 had sludge and fly ash as the main components. The sample T2 had similar trend as curves for T1 and T3, but with lower values. T2 had the main component fly ash (ground and unground; 50/50 %).

The capillary action (in cm) on the surface of investigated samples was high in T1 and T3 (Fig. 1), but during assessment according to the percentage of the weight of capillarity after 90 minutes the maximum values were observed in the samples T2 and T3 (samples containing original fly ash in the mixture).

The samples T4 and T5 had slow and steady progress of absorption, according to Figure 1. In terms of capillarity (in percent by weight, Tab. 5) T1, T4 and T5 had lower value (4%) of capillarity than T2, T3 (5-6%).

4 CONCLUSIONS

The results indicate the effect of ground fly ash for production of geopolymer mixtures. The properties of geopolymers were measured after 28 days of hardening. The durability properties, such as water absorption and capillarity, showed a decreasing trend with the increase of fly ash fineness. Hence, it is concluded that increasing the fineness of fly ash increases its reactivity, and, hence, grinding is an effective way to enhance the performance of fly ash. When the volume of the ground fly ash is increasing, it will fill the voids increasing thus the density and hence preventing water absorption. The samples with a higher density by utilization of ground fly ash for geopolymer mixtures caused increases of resulting compressive and flexural strength.

The treatment of raw materials may enhance some of geopolymers parameters, while deteriorating others. This affects not only the final parameters of geopolymers, but also technological parameters, e.g. consistency, compatibility, setting time, etc. Therefore any way of treatment and optimization of the input raw materials is a result of looking for limiting values and interactions, followed by setting of priorities and acceptance of compromises.

Practical implications

The obtained results of selected properties of geopolymers with different portions of ground fly-ash show that the portion of the original and ground fly ash influences the final properties of the geopolymer. The best results were identified in the recipe of T4 (70% of ground fly ash, 30% sludge). Fly ashes and other mechanically modified secondary raw materials (slag, sludge, waste glass, ceramic waste etc. ...) improved the possibilities of use of secondary raw materials, and of their reuse in new building materials. The aim of research was oriented on the use of mechanically modified fly ash used as a microfiller in mixtures, to serve as a protective coating (plaster).

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